

Thermodynamic States of Gas

For any gas can describe state via

N = number of particles

V = volume of gas

P = pressure of gas

T = temperature of gas

Will consider situations where pressure is same everywhere. Also where temperature is same everywhere.

An equilibrium state is one for which each variable takes on one value for entire system.
 "Equilibrium thermodynamics"

Thermodynamic States of Other Systems

List variables that describe state of system

e.g. Nuclear spins

N = number of spins

\vec{M} = magnetization

T = temperature

A thermal equilibrium state is one for which each variable takes one value throughout system

e.g. $N = 10^{20}$

$\vec{M} = 60 \text{ A m}^2 \hat{z}$

$T = 500 \text{ K}$

Temperature

Want a definition of temperature. Want a definition that avoids relying on:

1) human sensation

2) a particular apparatus

One can produce an intuitive definition by considering interacting systems

Example: (Interacting Systems):

System A: Balloon holds gas at "room temperature"

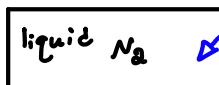
System B: Pool of liquid nitrogen at boiling point of liquid nitrogen

Initially:

- Systems are isolated from each other

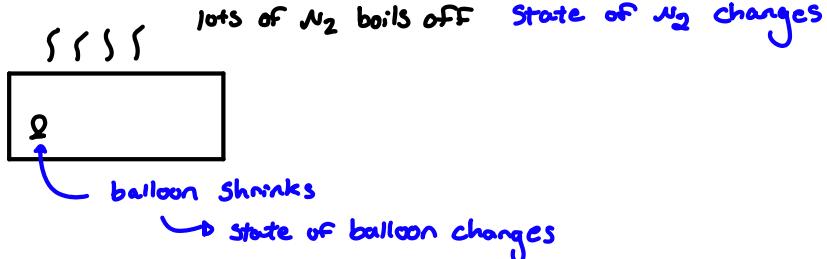


In an equilibrium state



In an equilibrium state

- Immerse balloon



Because there is a change when they come into contact, the two systems were not in thermal equilibrium with each other initially.

In general:

Systems A and B are in thermal equilibrium if, once they are placed in thermal contact with each other, their states do not change

Initial definition of temperature:

Systems A and B are at same temperature iff they are in thermal equilibrium with each other

Requires: Zeroeth law of thermodynamics

If systems A and B are in thermal equilibrium with each other and systems A and C are in thermal equilibrium with each other then systems B and C are in thermal equilibrium with each other

Example: A = small thermometer

B = water

C = alcohol

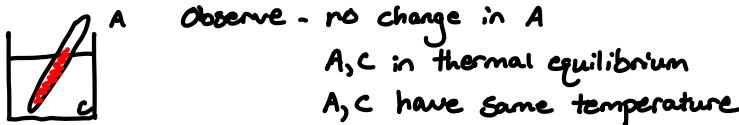
Consider two operations:

① Put A in B



reach equilibrium \rightarrow large change in A, negligible change in B
 \Rightarrow eventually A in thermal equilibrium with B
 \Rightarrow A, B have same temperature

② Put A in C



Observe - no change in A
A, C in thermal equilibrium
A, C have same temperature

Zeroeth Law

\Rightarrow B, C in thermal equilibrium

\Rightarrow B, C have same temperature

In general

Two systems have same temperature (\Leftrightarrow) they are in thermal equilibrium with each other
Two " " different temps (\Leftrightarrow) " " not in thermal equilibrium with each other

Historical thermometer:

- dilute constant volume gas thermometer
- notion of absolute minimum temperature
- Scale: kelvin (K)

Equations of State

Consider any gas:

Describe state using:

N, V, P, T

Not all independent. They must be related by some equation
↳ (pressure) equation of state

Equation of state depends on system. Examples:

1) Ideal gas

Sufficiently dilute then

Ideal gas law $\rightarrow PV = NkT$ ← kelvin

$k = 1.38 \times 10^{-23} \text{ J/K}$ → Boltzmann's constant

N → Number of particles

Scheme:

List Variables: N, V, T, P \longleftrightarrow Equation of state $PV = NkT$

only three variables are independent

one possibility: N, T, V independent

$$P = \frac{NkT}{V}$$

Another: N, V, P independent

$$T = \frac{PV}{Nk}$$

2) Van der Waals gas

- considers interactions between molecules, Volume occupied by molecules

:

$$\left[P + \frac{N^2 a}{V^2} \right] \left[V - Nb \right] = NkT$$

$a > 0$ \hookrightarrow depends on gas

depends on gas

Geometrical Representation of States

Can use four dimensional space to represent states of a gas

N, V, P, T

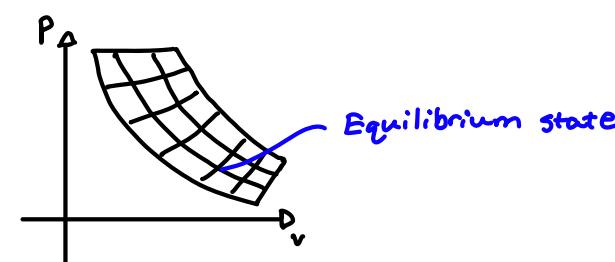
To Simplify suppose N is fixed. Only need three variables
 P, V, T

Equation of state $PV = NkT$

$$P = \frac{NkT}{V} \quad P = P(V, T) = \frac{NkT}{V}$$

gives two dimensional surface in space

Equilibrium states are represented by a point in (P, V, T) space on surface

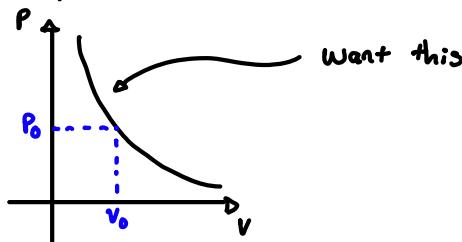


Determination of equation of stateGas: Variables P, V, N, T Want $P = P(V, N, T)$ e.g. ideal gas $P = \frac{NkT}{V}$

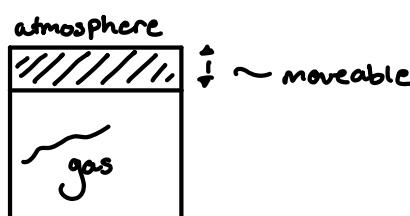
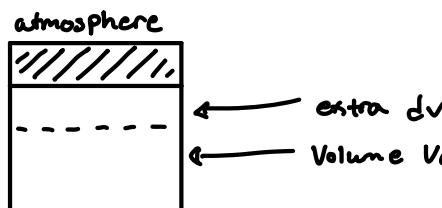
Consider:

- * Possible experimental measurements and data
- * Mathematics that manipulates data to get $P = P(V, N, T)$

Mathematical idea

Suppose that temperature is fixed. Want to know how P depends on V .Determine one equilibrium state (location on curve) P_0, V_0, N, T_0

- ↳ Keep temperature fixed at T_0 and determine how one variable (e.g. P) varies as the other varies (e.g. V). Slope (derivative) of curve
- ↳ Use slope information to determine (via integration) to get P as V at this temperature.
- ↳ Repeat procedure allowing T to vary while say P is constant and observe $V \rightsquigarrow$ slopes.

Experimental SchemeStep 1: Keep pressure fixed at P_0 . observe temperature T_0 , volume V_0 Step 2: Vary temperature $T_0 \rightarrow T_0 + \Delta T$
observe volume change $V_0 \rightarrow V_0 + \Delta V$ 

Step 3: Relate dV to dT . gives

$$\frac{dV}{dT} = \text{observed quantity}$$

Step 4: Integrate to get V as a function of T at constant P_0

Convention:

$$dV = \alpha V dT$$

where

$\alpha \equiv$ isobaric thermal expansion coefficient

How to extract equation of state?

Want $V = V(T, P)$

$$dV = \frac{\partial V}{\partial T} dT + \frac{\partial V}{\partial P} dP$$

Here P is constant $\Rightarrow dP = 0$

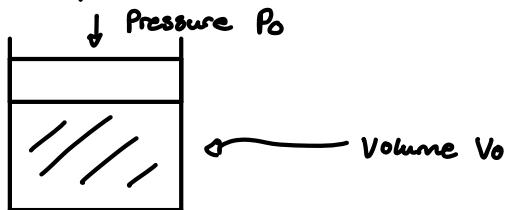
$$dV = \frac{\partial V}{\partial T} dT \Rightarrow \alpha V = \frac{\partial V}{\partial T} \Rightarrow \alpha = \frac{1}{V} \frac{\partial V}{\partial T}$$

Scheme:

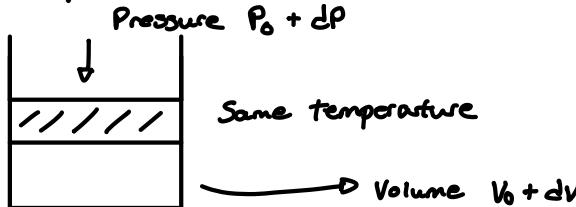
Know how α depends on V, T $\alpha = \alpha(V, T) \rightarrow \alpha = \frac{1}{V} \frac{\partial V}{\partial T}$ means integrate to get how V depends on T at constant P

Thermal expansion coefficient only gives partial information about equation of state (only curves for $P = \text{constant}$). Need to know how V varies versus P to complete picture.

① Keep temperature fixed at T_0



② Increase pressure $P_0 \rightarrow P_0 + dP$. observe volume change $V_0 \rightarrow V_0 + dV$



③ Relate dV to $dP \rightarrow$ gives $\frac{\partial V}{\partial P} = \text{observed quantity}$

④ Integrate to relate V to P and T .

Conventions

$$dV = kVdP$$

$k \equiv$ isothermal compressibility

$$K = -\frac{1}{V} \frac{\partial V}{\partial P} \quad \text{most materials: } K > 0 \text{ since } \frac{\partial V}{\partial P} < 0$$

most materials: $K > 0$ since $\frac{\partial V}{\partial P} < 0$

In previous example

e.g. $\alpha = \frac{1}{T} \Rightarrow V = T e^{f(P)}$ $f(P)$ \leftarrow unknown

Now

$$\frac{\partial V}{\partial P} = T e^{f(P)} \frac{df}{dP}$$

$$\frac{1}{V} \frac{\partial V}{\partial P} = \frac{T e^{f(P)}}{T e^{f(P)}} \frac{df}{dP}$$

$$-\frac{1}{V} \frac{\partial V}{\partial P} = -\frac{df}{dP}$$

$$K = -\frac{df}{dP}$$

Now can get f and complete equation of state.

Scheme:

use experiments to determine isobaric thermal expansion coefficient $\alpha = \alpha(V, T)$ and isothermal compressibility $K = K(V, P)$. Know one state P_0, V_0, T_0

$$\frac{\partial V}{\partial P} = -VK \text{ and } \frac{\partial V}{\partial T} = V\alpha \longrightarrow \text{Integrate to determine } P = P(V, T)$$

Thermodynamic Processes

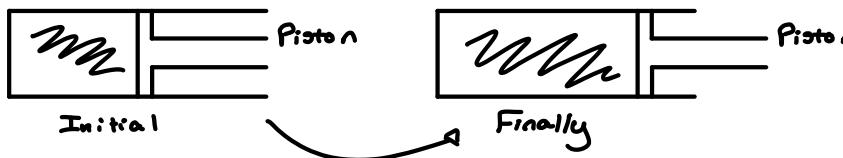
- thermodynamic system changes from one equilibrium state to another state..
- will consider:
 - 1) energy changes and flows in such processes
 - 2) which processes are possible

Two types of processes:

- * Quasistatic processes
- * non-quasistatic processes

Example: Slow expansion of a gas

Gas in a cylinder



Let gas expand slowly

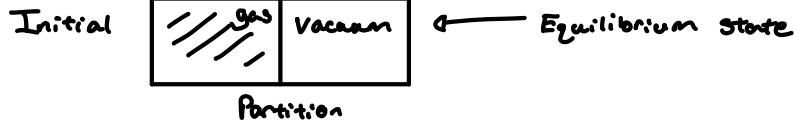
If expansion is slow enough then at each instant well defined: P, V, N, T

So

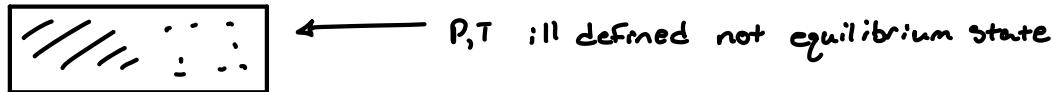
- * At every instant gas is in some thermal equilibrium state
- * passes through a succession of thermal equilibrium states

↳ Quasistatic

Example: Free expansion: Non quasistatic process



During Remove partition

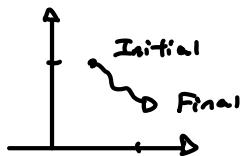


Finally



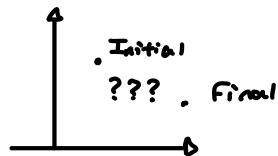
Quasistatic

- At every instance in some equilibrium state
- * curve on P, V, T Surface
- * Can do PV diagram



Non-Quasistatic

- At some instant not in an equilibrium state
- * not on P, V, T Surface
- * no curve in PV diagram



Processes and Energy

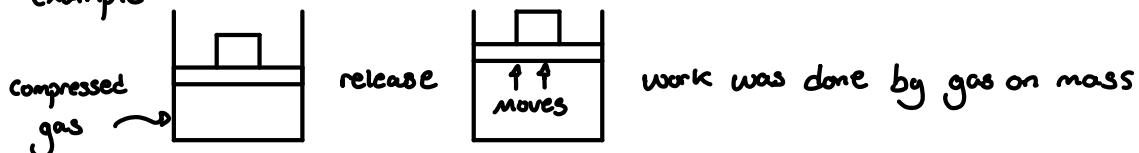
1) Gas expansion



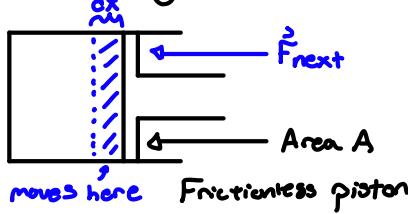
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Work + thermodynamics

example



Consider a gas in a cylinder



- 1) Push out constant velocity with constant external force \vec{F}_{ext} with constant external force \vec{F}_{ext}
- 2) Piston moves infinitesimal distance dx
- 3) Pressure stays constant at P .
In general $W = \vec{F} \cdot d\vec{r}$
Work done by external force on gas

$$W = F_{\text{ext}} dx$$

$$\text{and } F_{\text{ext}} = F_{\text{gas}} = PA$$

$$W = P A dx \quad \Rightarrow \quad W = -P dV$$

$\underbrace{}$
 $-dV$

For a non-infinitesimal process

The work done on a gas in any quasistatic process is

$$W = - \int_{\text{initial}}^{\text{final}} P(V) dV$$

where $P(V)$ is pressure during stages of the process

Note:

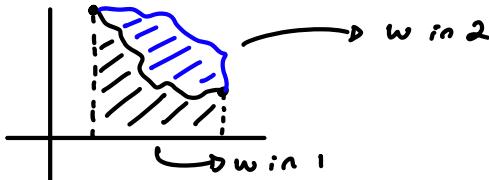
- 1) True for any gas
- 2) work done by gas is negative of work done on gas
- 3) Work = -area under curve on a PV diagram.

Note:

The work done on a thermodynamic system depends on

- 1) initial + final states of System
- 2) the nature process

Work done from same initial to same final state can be different for different processes



Energy in thermodynamics

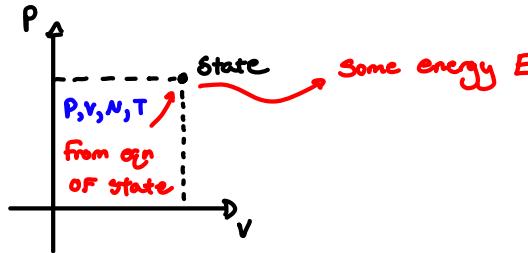
- ignore energy (KE, PE) associated with bulk motion.
- there must be some energy internal to the system (e.g. gas) that relates work done on the system.

General postulate:

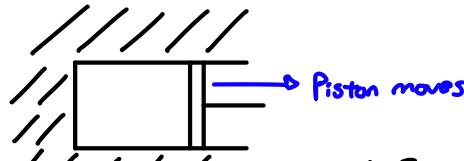
For any thermodynamic system there exists an internal (thermal) Energy, E which depends only on the State of the System



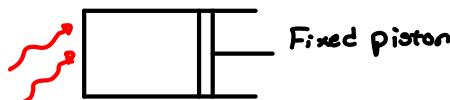
There is a function : $E = E(P, V, T, N)$ that only depends on system state



Consider two processes



Insulated from surroundings gas expands. Work on: $W < 0$ no other way for energy to enter/leave



Heat energy Can't supply energy by placing gas in contact with another system but $W=0$.

Additional energy in form of heat, Q .

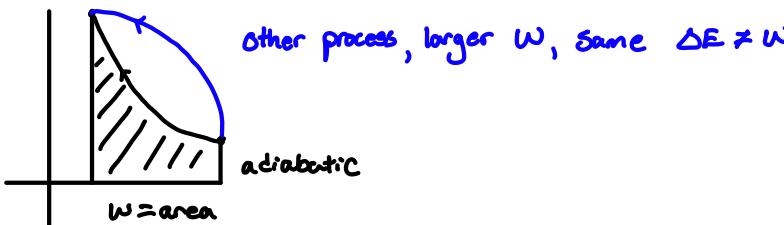
First Law of Thermodynamics

If heat flow is zero (System is isolated from surrounding) then process is adiabatic

For an adiabatic process

$$\Delta E = W$$

Where W = work done on system



Suppose a system undergoes a process then:

$$\Delta E = W + Q$$

Where $\Delta E = E_f - E_i$

W = work done on system

Q = heat entering system

Note:

- 1) Heat is associated with a process, not a state
- 2) Heat depends on process (even for some initial / final states)

Energy equation of State

Depends on system: Ideal gas $E = \frac{3}{2} NkT$
(monatomic)

$$V.d. \text{ Waals } E = \frac{3}{2} NkT - \frac{N^2 a}{V}$$

First Law of Thermodynamics

Specify System and Variables

Monoatomic ideal gas: P, V, T, N

→ Equation of State that relates variables

$$\text{Monoatomic ideal gas } PV = NkT$$



Macroscopic work can be done Quasistatic process can compute this

$$\text{Gas} = - \int P dv$$



System has internal Energy E only depending on state.

$$\text{Monoatomic ideal gas } E = \frac{3}{2} NkT$$

First law of thermodynamics

For any process

$$\Delta E = W + Q$$

where Q = heat supplied

Determining energy equation of state

- Via experiment and some math?

- Recall how to get $PV = NkT$

Measure: thermal expansion

$$\text{Coefficient: } \alpha = \frac{1}{V} \frac{\partial V}{\partial T}$$

→ Extract $\frac{\partial V}{\partial T}, \frac{\partial V}{\partial P}$

Isothermal compressibility

$$\kappa = \frac{-1}{V} \frac{\partial V}{\partial P}$$

→ Integrate give $V = V(T, P)$

→ Invert $P = P(V, T)$

For energy equation of state:

Measurements eventually give

$$\frac{\partial E}{\partial T}, \frac{\partial E}{\partial V}, \dots$$

→ Integrate to get

$$E = E(T, V, \dots)$$

Derivatives of E are important

e.g. ideal gas

$$E = \frac{3}{2} PV$$

$$E = \frac{3}{2} NkT$$

Derivatives depend on what variables are regarded as independent

Functions of multiple variables

gas. e.g.

$$F = \alpha \frac{v^2}{T} = F(v, T)$$

↑
constant

regarding: v, T as independent

But $PV = nRT$

$$\Rightarrow F = \alpha \cdot \frac{n^2 k^2 T}{P} = F(P, T)$$

P, T as independent

$$F = \alpha \cdot \frac{NkV}{P} = F(P, V)$$

P, V as independent

In example:

What are independent variables

$$\begin{array}{l} P, T \rightarrow \text{write } F = F(P, T) \rightarrow \text{differentiate w.r.t } T \rightarrow \text{result } \left(\frac{\partial F}{\partial T}\right)_P = \frac{1}{P} \\ V, T \rightarrow F(V, T) \longrightarrow \dots \dots \longrightarrow \left(\frac{\partial F}{\partial T}\right)_V = 0 \end{array}$$

General Scheme:

Decide on independent variables x, y, z



Express F in terms of independent variables

$$F = F(x, y, z, \dots)$$



Derivative of w.r.t x is

$$\left(\frac{\partial F}{\partial x}\right)_{y, z, \dots}$$

independent variables

Energy equation of state?

Consider N fixed

Assume V, T are independent

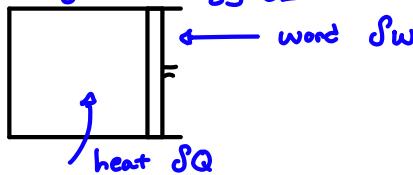


Get $\left(\frac{\partial E}{\partial r}\right)_V$ and $\left(\frac{\partial E}{\partial r}\right)_T$ and integrate to get E

Heat Capacities

Need to make system undergo an infinitesimal quasistatic process

Change in energy dE



Small changes in Variables

$$dv =$$

$$dp = \text{small change in } P$$

$$dT =$$

$$dE =$$

$\left\{ \begin{array}{l} \text{Small process} \\ \delta W = \text{small work} \\ \delta Q = \text{small heat} \end{array} \right.$

First law

$$dE = \delta W + \delta Q$$

for any gas
 $\delta W = -PdV$

$$\Rightarrow dE = -PdV + \delta Q$$

Calculus : (Suppose V,T independent)

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

so

$$\left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV = -PdV + \delta Q$$

$$\delta Q = \left(\frac{\partial E}{\partial T} \right)_V dT \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] dV \text{ if } V, T \text{ are independent.}$$

expt :

keep volume fixed

Add heat δQ

Measure temperature change dT

math says

$$\delta Q = \left(\frac{\partial E}{\partial T} \right)_V dT$$

$$\Rightarrow \left(\frac{\partial E}{\partial T} \right)_V = \frac{\delta Q}{dT}$$

Can always do :

Regard , T,V, as independent

Then

$$\delta Q = C_V dT + [\text{Something}] dV \text{ where } C_V \equiv \text{heat capacity at constant } V$$

Here

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

Suppose T,P are independent . Then can write :

$$\delta Q = C_P dT + [\text{Something}] dP \text{ where coefficient of } dT \\ \text{i.e. } C_P \equiv \text{heat capacity at constant pressure}$$

2-6-20

Heat Capacities + Energy

Fixed Volume

heat $\delta Q \Rightarrow$ measure temp change dT heat $\delta Q \Rightarrow$ measure temperature change dT

heat capacity at constant volume

$$C_V = \frac{\partial Q}{\partial T}$$

heat capacity at constant pressure

$$C_P = \frac{\partial Q}{\partial T}$$

First law

$$dE = \delta Q - PdV$$

Calculus: $dE = \left(\frac{\partial E}{\partial x}\right)_y dx + \left(\frac{\partial E}{\partial y}\right)_x dy$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V, \quad C_P = \left(\frac{\partial E}{\partial T}\right)_P + P \left(\frac{\partial V}{\partial T}\right)_P, \quad C_P = C_V + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial T}\right)_V + P \right]$$

Ex: Ideal Gas

Want $E = E(V, T)$

Have:

1) Equation of State

$$PV = NkT \rightarrow V = \frac{NkT}{P}, \quad P = \frac{NkT}{V}$$

2) Experiment to get C_P, C_V

Experiments indicate:

For an ideal gas (at moderate temps)

$$C_P = C_V + Nk$$

and

$$C_V = fNk$$

where $f = 3/2$ monoatomic

$f = 5/2$ diatomic

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = fNk$$

$$\left(\frac{\partial E}{\partial T}\right)_V = fNk$$

and

$$C_P = C_V + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right]$$

$$C_V + Nk = C_V + \frac{Nk}{P} \left[\left(\frac{\partial E}{\partial V}\right)_T + P \right] : \left(\frac{\partial V}{\partial T}\right)_P = \frac{Nk}{P}$$

$$Nk = \frac{Nk}{P} \left(\frac{\partial E}{\partial V}\right)_T + Nk \Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = 0$$

$$\left(\frac{\partial E}{\partial T}\right)_V = fNk : E = \int fNk dT, \quad E = fNkT + g(V)$$

$$\text{Then } \left(\frac{\partial E}{\partial T}\right)_V = 0 + \frac{dg}{dT} = 0 \Rightarrow g = \text{constant}$$

$$E(V,T) = f_{NK} T + \text{const}$$

Convention : when $T \rightarrow 0$, $E \rightarrow 0 \Rightarrow E = f_{NK} T$

when V, T are two variables :

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V : C_P = C_V + \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right]$$

What if P, T are two variables :

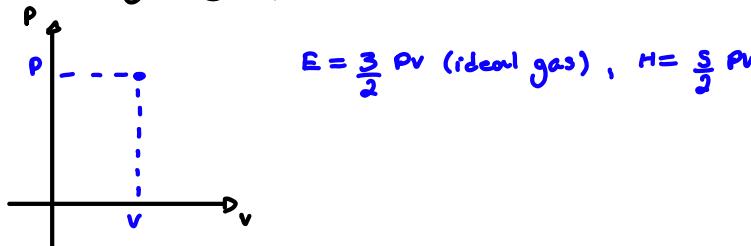
$$C_P = \left(\frac{\partial E}{\partial T} \right)_P + \left(\frac{\partial V}{\partial T} \right)_P : C_V = C_P - P \left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial E}{\partial P} \right)_T \left(\frac{\partial P}{\partial T} \right)_V$$

Quantity that represents energy situation better for variables P, T .

Enthalpy

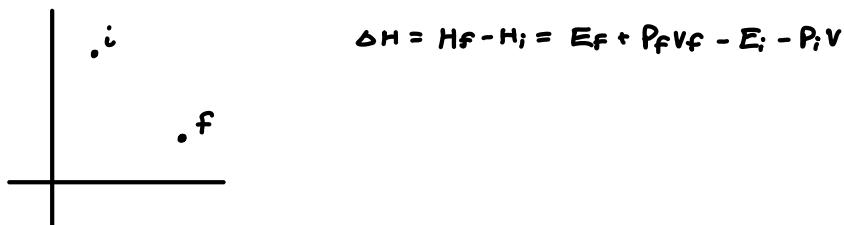
Define enthalpy as : $H = E + PV$

1) enthalpy only depends on state of system i.e. on P, V, N, T : $H = H(P, V, T)$
 $H = H(V, N, T)$



2) Units : Joules

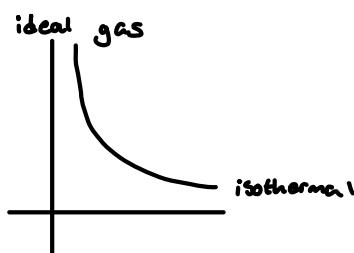
3) Changes in enthalpy can be determined for any process



4) well suited to describe processes where P is constant.

Adiabatic Process

- * no heat enters or leaves
- * Adiabatic vs. isothermal



isothermal $T = \text{const}$
 $PV = \text{const}$
 $P = \frac{1}{V} \times \text{constant}$

Adiabatic:

$$\Delta E = \cancel{Q} + w$$

$$\Delta E = +w$$

Compress:

$$w > 0$$

$$\Delta E > 0$$

a) $dE = \cancel{dQ} - PdV$
 $dE = -PdV$

$$\left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV = -PdV$$

$$C_V dT = -PdV$$

b) $C_V \left(\frac{\partial T}{\partial V} \right)_P dV + C_V \left(\frac{\partial T}{\partial P} \right)_V dP = -PdV$

$$\left[C_V \left(\frac{\partial T}{\partial V} \right)_P + P \right] dV = -C_V \left(\frac{\partial T}{\partial P} \right)_V dP$$

$$\left(\frac{\partial T}{\partial V} \right)_P = \frac{1}{(\partial V / \partial T)_P} \quad \dots \quad \frac{C_P}{C_V} P dV = -V dP$$

$$\cancel{\gamma} P dV = -V dP$$

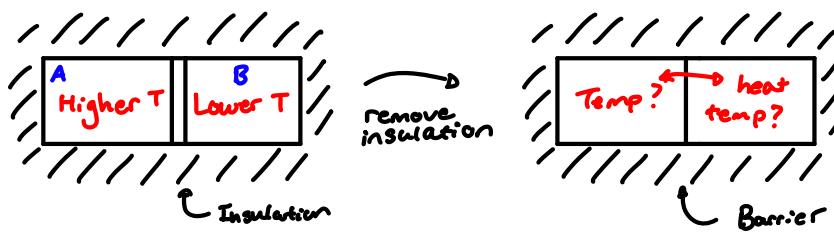
$$\cancel{\gamma} \frac{dV}{V} = -\frac{dP}{P} : \cancel{\gamma} \int \frac{dV}{V} = - \int \frac{dP}{P} : \cancel{\gamma} \ln(V) = -\ln(P) + \text{const} \rightarrow V^{\cancel{\gamma}} = \frac{\text{const}}{P}$$

2-11-20

Possible Thermodynamic Processes

First law does not say which processes will occur

Example: Two gases



which way does heat flow? What does the First law say?

For A:

$$\Delta E_A = Q_A + W_A$$

For B:

$$\Delta E_B = Q_B + W_B$$

Volumes constant $w_A = 0$

$$w_B = 0$$

Energy Conserved

$$\Delta E_A + \Delta E_B = 0 \Rightarrow Q_A + Q_B = 0$$

$$\Rightarrow Q_B = -Q_A$$

Doesn't say whether $Q_A > 0$ or $Q_A < 0$

First law doesn't say which of these occurs:

- 1) Heat goes from A to B
- 2) " " " B to A

First law still useful:

e.g. Suppose C_V independent of T, V

$$\delta Q = C_V dT + [\dots] dV$$

$$\delta Q = C_V dT$$

$$Q = \int \delta Q = \int C_V dT$$

$$Q = C_V \Delta T$$

$$Q_A = C_{V,A} \Delta T_A = C_{V,A} (T_{A,F} - T_{A,I})$$

$$Q_B = \dots = C_{V,B} (T_{B,F} - T_{B,I})$$

$$Q_B = -Q_A$$

$$C_{V,B} (T_{B,F} - T_{B,I}) = -C_{V,A} (T_{A,F} - T_{A,I})$$

Usual observation is that eventually $T_{A,F} = T_{B,F}$ ← First law doesn't say anything about temps

- ↳ Gas B temp rises $Q_B > 0$
 Gas A temp drops $Q_A < 0$

Want another law of Thermodynamics to say which process occurs.

The Second Law of Thermodynamics

Requires a new variable: entropy

Any equilibrium state:

e.g. gas P, V, N, T



There exists an entropy function → Thermodynamic variables can be determined from entropy by differentiation

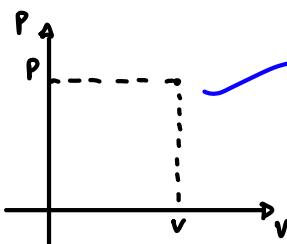
$$S = S(P, V, N, T)$$



Processes that occur satisfy $\Delta S \geq 0$

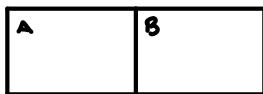
Statistical Physics

For any thermodynamic system there exists a macroscopic quantity, entropy, denoted by S . It only depends on state.



Temperature via equation of state $T = \frac{PV}{Nk}$, energy $E = \frac{3}{2} Nk$, entropy $S = ??$ function of P, V, N, T

Consider two systems



	System A	System B	both	
Particles	N_A	N_B	$N = N_A + N_B$	variables that add for two systems are called extensive, others intensive (T, P)
Volume	V_A	V_B	$V = V_A + V_B$	
Energy	E_A	E_B	$E = E_A + E_B$	
Entropy	S_A	S_B		

We will require:

$$S = S_A + S_B$$

$\downarrow \quad \curvearrowright$

$$S_B(P_B, V_B, T_B, N_B)$$
$$S_A(P_A, V_A, N_A, T_A)$$

Consider processes that involve A, B



Can exchange energy, particles, ...

Light

Particles $N_{Ai}, N_{Bi}; \quad N_{Af} \quad N_{Bf}$
Energy $E_{Ai}, E_{Bi}; \quad \dots \dots \dots$

Can be constraints: e.g. no particles lost

$$N_{Af} + N_{Bf} = N_{Ai} + N_{Bi}$$

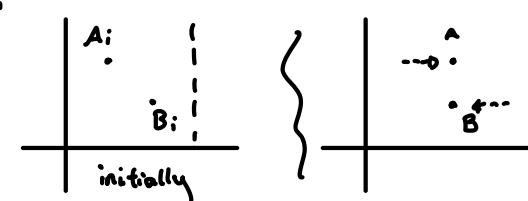
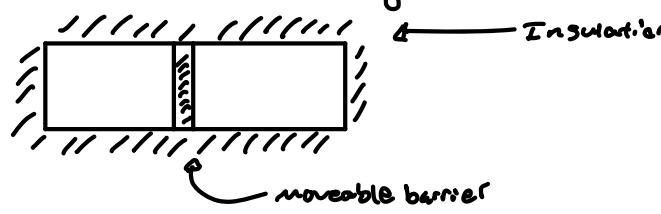
or maybe no energy lost

$$E_{Af} + E_{Bf} = E_{Ai} + E_{Bi}$$

which of these occurs depends on process

For any isolated system, the equilibrium state of the system is such that it will have the maximum entropy possible given constraints

Second Law of Thermodynamics

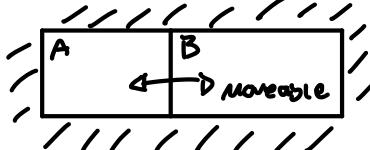


Also:

For any process $\Delta S = S_f - S_i \geq 0$
Process is reversible

Pressure + temperature from entropy

Two systems that are isolated from their surroundings but can interact with each other



- * Number of particles in each is fixed
- * V_A, V_B can change : $V = V_A + V_B = \text{const.}$
- * E_A, E_B " " : $E = E_A + E_B = \text{const.}$

2.13 - 20

Second Law of Thermodynamics, Entropy, Temperature

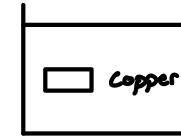
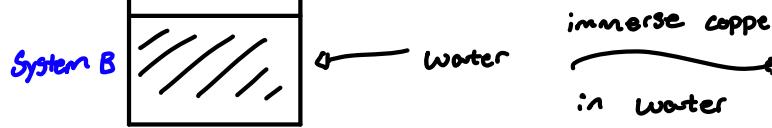
The equilibrium state of any isolated system will be the state for which the entropy is a maximum subject to any constraints on system.

Some implications:

- 1) Thermodynamic processes: Two systems initially isolated from each and then brought into contact.

System A

copper



Combined system A+B isolated from surroundings.

Has some total entropy S ;

Energy exchanged. Total entropy S_F

For an isolated system \rightarrow Quasistatic process $dS \geq 0$

$$\Delta S = S_F - S_i$$

in any process

- 2) Equilibrium between systems :

If energy can be exchanged then equilibrium state satisfies $\left(\frac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} = \left(\frac{\partial S_B}{\partial E_B}\right)_{V_B, N_B}$

If Volume can change $\left(\frac{\partial S_A}{\partial V_A}\right)_{E_A, N_A} = \left(\frac{\partial S_B}{\partial V_B}\right)_{E_B, N_B}$

- 3) Thermodynamic Temperature

$$T = \frac{1}{(\partial S / \partial E)_{V, N}}$$

This plus second law

\Rightarrow 1) Temps of two systems in equilibrium are equal

2) Energy flows from higher to lower temperature system

Units of Entropy

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T} : \frac{\text{Units of } S}{J} = \frac{1}{K} \therefore \text{Units of } S = \frac{J}{K}$$

Thermodynamic Pressure

Interacting Systems whose Volumes can change

- In equilibrium in this case pressures will be same.
- Larger pressure system gains volume.

$$P \text{ related } \left(\frac{\partial S}{\partial V}\right)_{E,N}$$

As P increases $\left(\frac{\partial S}{\partial V}\right)_{E,N}$ increases.

$$P = T \left(\frac{\partial S}{\partial V}\right)_{E,N} \text{ need } S = S(E, V, N)$$

Measuring entropy changes

First law:

$$dE = \delta Q - PdV : \text{Fixed } N$$

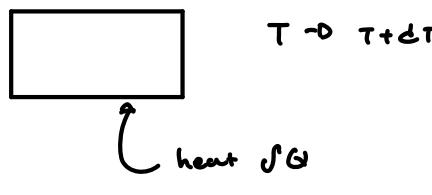
$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV$$

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV = \delta Q - PdV : \longrightarrow \frac{1}{\left(\frac{\partial S}{\partial E}\right)_{V,N}} = T$$

$$TdS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV = \delta Q - PdV$$

$$dS = \frac{1}{T} \delta Q - \frac{1}{T} \left[P + \left(\frac{\partial E}{\partial V}\right)_{S,N} \right] dV$$

Constant Volume process



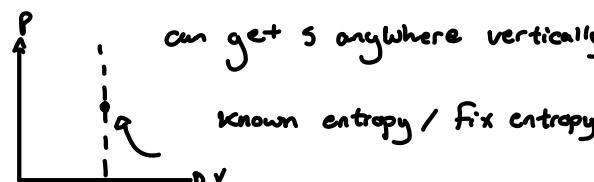
Then for Constant Volume process

$$dS = \frac{1}{T} \delta Q$$

$$dS = \int \frac{1}{T} \delta Q$$

Also for constant Volume process

$$\delta Q = C_V dT : dS = \int \frac{C_V}{T} dT$$



Fundamental Thermodynamic Identity Part 1

$$ds = \left(\frac{\partial s}{\partial E} \right)_{V,N} dE + \left(\frac{\partial s}{\partial V} \right)_{E,N} dV$$

$$= \frac{1}{T} dE + \frac{P}{T} dV$$

$$TdS = dE + PdV \quad \therefore \quad dE = TdS - PdV$$

note:

$$dE = \left(\frac{\partial E}{\partial S} \right)_V dS + \left(\frac{\partial E}{\partial V} \right)_S dV$$

$$\Rightarrow T = \left(\frac{\partial E}{\partial S} \right)_V \Rightarrow T = \frac{1}{(\partial S / \partial E)_V}$$

$$-P = \left(\frac{\partial E}{\partial V} \right)_S \quad \therefore \quad P = - \left(\frac{\partial E}{\partial V} \right)_S$$

Entropy and heat flow

note:

$$dE = \delta Q - PdV$$

and

$$dE = TdS - PdV$$

For any quasistatic process:

$$\int Q = TdS \Rightarrow ds = \frac{1}{T} \int Q$$

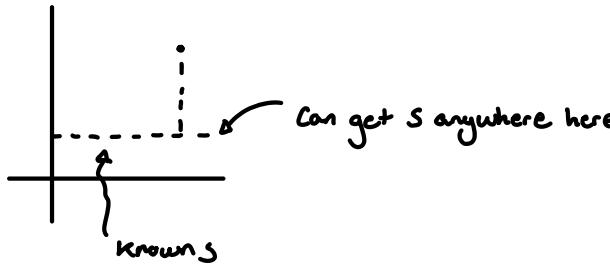
any process:

$$Q = \int TdS \text{ and } \Delta S = \int \frac{1}{T} \int Q$$

If pressure is constant

$$\delta Q = C_p dT$$

$$\Delta S = \int \frac{C_p}{T} dT \text{ Constant pressure}$$



Variable Particle Number

Two systems that interact

$$S = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B)$$

assume $E = E_A + E_B = \text{const}$

:

$$N = N_A + N_B = \text{const}$$

:

in equilibrium

$$\left(\frac{\partial S_A}{\partial N_A}\right)_{E_A, V_A} = \left(\frac{\partial S_B}{\partial N_B}\right)_{E_B, V_B}$$

Chemical potential for system

$$\mu = -T \left(\frac{\partial S}{\partial N}\right)_{E, V}$$

Two systems are in equilibrium if chemical potentials are same

2-18-20

Chemical potential

Two systems that can exchange particles. In equilibrium with each other

$$\Rightarrow \left(\frac{\partial S}{\partial N}\right)_{E, V}$$

is same for both

Chemical potential

$$\mu = -T \left(\frac{\partial S}{\partial N}\right)_{E, V}$$

In equilibrium if systems can exchange particles then chemical potential is same

Suppose volumes of two systems are fixed.

$$\begin{aligned} dS &= dS_A + dS_B = \left(\frac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} dE_A + \left(\frac{\partial S}{\partial N_A}\right)_{E_A, V_A} dN_A + \left(\frac{\partial S}{\partial N_B}\right)_{E_B, V_B} dN_B + \text{Similar for } B \\ &= \frac{1}{T_A} dE_A - \frac{\mu_A}{T_A} dN_A + \frac{1}{T_B} dE_B - \frac{\mu_B}{T_B} dN_B \end{aligned}$$

Total energy const: $dE_B = -dE_A$

Total particles: $dN_B = -dN_A$

$$dS = \left(\frac{1}{T_A} - \frac{1}{T_B}\right) dE_A - \left(\frac{\mu_A}{T_A} - \frac{\mu_B}{T_B}\right) dN_A$$

Suppose temps are same. $T_A = T_B = T$

$$dS = -\frac{1}{T} (\mu_A - \mu_B) dN_A \geq 0$$

$$-(\mu_A - \mu_B) dN_A \geq 0$$

if $\mu_A \geq \mu_B \Rightarrow dN_A < 0$ Particles go from larger to smaller chemical potential
 $\mu_A \leq \mu_B \Rightarrow dN_A > 0$

Fundamental thermodynamic identity

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN$$

$$dE = TdS - PdV + \mu dN : \text{Note } TdS = \delta Q$$

$$dE = \delta Q - PdV + \mu dN$$

useful for :

1) Energy changes

$$\Delta E = \int \delta Q - \int PdV + \int \mu dN$$

heat in work on (Energy added when one adds particles)

2) Relates Quantities via derivatives

$$dE = \left(\frac{\partial E}{\partial S}\right)_{V,N} dS + \left(\frac{\partial E}{\partial V}\right)_{S,N} dV + \left(\frac{\partial E}{\partial N}\right)_{S,V} dN$$

$$\left(\frac{\partial E}{\partial S}\right)_{V,N} = T, \quad \left(\frac{\partial E}{\partial V}\right)_{S,N} = -P, \quad \left(\frac{\partial E}{\partial N}\right)_{S,V} = \mu$$

Entropy of an ideal gas

want

$$S = S(T, V, N)$$

start with :

Fundamental thermodynamic identity

$$S = S(E, V, N)$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$

$$\left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{P}{T}$$

$$\left(\frac{\partial S}{\partial N}\right)_{V,E} = \frac{\mu}{T}$$

equations of state :

$$PV = NkT, \quad E = fNkT = fPV$$

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{fNk}{E}, \quad \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk}{V}, \quad \left(\frac{\partial S}{\partial N}\right)_{E,V} = -\frac{fNk}{E} \mu$$

will get how S depends on T, V but not N .

$$\int \left(\frac{\partial S}{\partial E}\right)_{V,N} dE = \int \frac{fNk}{E} dE : S = fNk \ln(E) + g(V, N)$$

$$\left(\frac{\partial g}{\partial v}\right)_{E,N} = 0 + \left(\frac{dg}{dv}\right)_N = \frac{NK}{V} \quad : \quad \left(\frac{\partial g}{\partial v}\right)_N = \frac{NK}{V}$$

$$\int \left(\frac{\partial g}{\partial v}\right)_N dv = \int \frac{NK}{V} dv$$

$$g(v, N) = NK \ln(v) + h(N)$$

$$S = f_{NK} \ln(E) + NK \ln(v) + h(N)$$

" $S(E, v, N)$

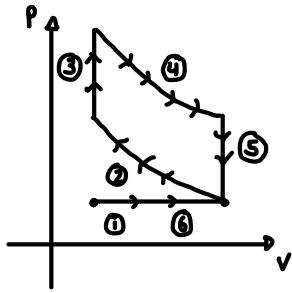
$$\begin{aligned} S &= f_{NK} \ln(f_{NK} T) + NK \ln(v) + h(N) \\ &= f_{NK} \left[\ln(T) + \ln(f_{NK}) \right] + NK \ln(v) + h(N) \\ &= f_{NK} \ln(T) + NK \ln(v) + \underbrace{f_{NK} \ln(f_{NK}) + h(N)}_{\tilde{h}(N) \text{ unknown fn of } N} \end{aligned}$$

$$S(T, v, N) = f_{NK} \ln(T) + NK \ln(v) + \tilde{h}(N)$$

Heat Engine

- * Converts heat into work via a thermodynamic system
- * System must go through a cycle and return to initial state

OTTO Cycles



Stage	V	P	T	ΔE	W	Q
① Intake	A	X	X	X	X	X
② Adiabatic	↓	↑	↑	+	+T	0
③ Const. vol.	const	↑	↑	+	0	+
④ Adiabatic	↑	↓	↓	-	-	0
⑤ Const. vol.	const	↓	↓	-	0	-
⑥ Expel	X	X	X	X	X	X

Thermal efficiency of engine

$$\eta = \frac{\text{Work done by gas in one cycle}}{\text{Heat supplied in one cycle}}$$

2-20-20

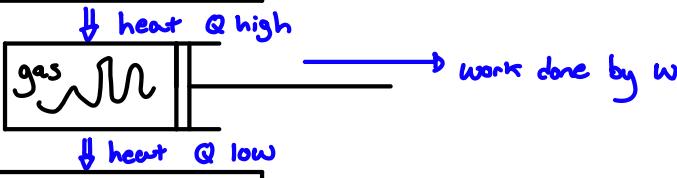
Heat Engines

- Convert heat to work
- require an intermediary
 - Thermodynamic System
 - e.g. ideal gas

must :

- 1) Operate in a cycle
 - State of gas at end of cycle is same as at beginning of cycle
- 2) Absorbs heat from an environment (reservoir (bath)) at higher temp
- 3) Ejects heat to another environment at a lower temperature

high temperature reservoir
Temperature T_{high}



$$\begin{aligned} W &= \text{magnitude of work done by gas} \\ Q_{\text{high}} &= \text{magnitude of heat entering gas} \\ Q_{\text{low}} &= " \text{ leaving gas} \end{aligned} \quad \left. \begin{array}{l} \\ \\ \end{array} \right\} \text{Per cycle}$$

First Law:

$$\begin{aligned} \Delta E &= Q + W_{\text{on gas}} \\ Q &= Q_{\text{high}} - Q_{\text{low}} - W \quad \curvearrowleft \text{ work by gas} \\ &\quad : \text{ State at end} = \text{ State at beginning} \end{aligned}$$

$$W = Q_{\text{high}} - Q_{\text{low}}$$

Efficiency:

$$\eta = \frac{W}{Q_{\text{high}}} = \frac{Q_{\text{high}} - Q_{\text{low}}}{Q_{\text{high}}} : \eta = 1 - \frac{Q_{\text{low}}}{Q_{\text{high}}}$$

Suppose a heat engine operates between two reservoirs, one at temp T_h and the other at temp T_L where $T_h \geq T_L$. Then the efficiency is bounded by:

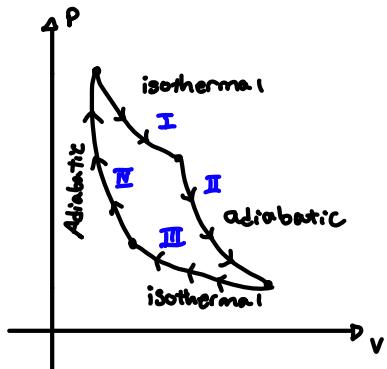
$$\eta \leq 1 - \frac{T_L}{T_h}$$

Carnot Cycle

Engine that attains max efficiency. Want

$$\Delta S = \Delta S_{\text{Engine}} + \Delta S_{\text{High}} + \Delta S_{\text{Low}} = 0$$

We will do this for an ideal gas



Carnot Cycle

Engine that attains max efficiency. Want
 $\Delta S = 0$

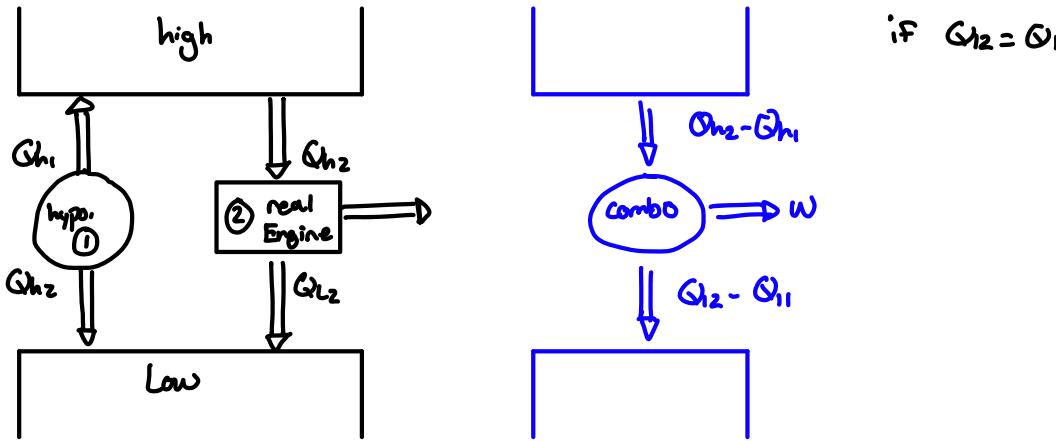
We will do this for an ideal gas

- 1) $PV = NkT$
- 2) $E = \frac{3}{2} NkT$
- 3) $PV^{\alpha} = \text{const}$
- 4) First Law
- 5) $\eta = 1 - \frac{Q_L}{Q_H}$

Connected Engines

- Can connect two engines \equiv a new single engine
- Can check hypothetical situations

Ex: Suppose a heat engine exists that transfers heat from low temp to high temp without any work.
Show can result in an engine with efficiency 1 regardless of temps.



2-25-20

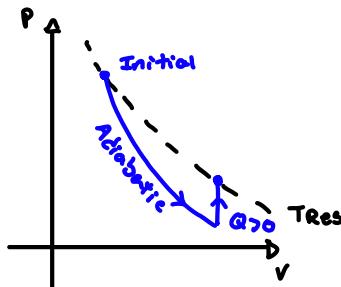
Helmholtz Free Energy

Consider a system interacting with environment and system undergoes a process with initial / final states at same temp as environment

Need

- 1) Temperature of reservoir is fixed at T_{Res}
- 2) System initial / final states have same Temperature as reservoir

e.g. Adiabatic expansion followed by constant volume process

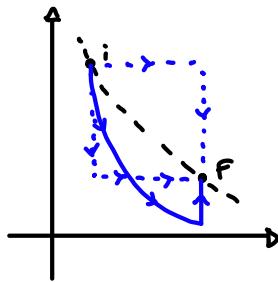


Quantity of interest is

$W_{\text{by}} = \text{Work by system}$

Want to know :

1) How much work can be extracted?



W_{by} depends on process.
Many possibilities

a) Is there some quantity so that
 $W_{by} \leq \Delta$ quantity \rightarrow only depends on state

Second Law:

$$\Delta S_{tot} = \underbrace{\Delta S}_{\text{System}} + \Delta S_{res.} \geq 0$$

If a system is in contact with reservoir and the system undergoes a process where initial / Final temperatures are the same as the reservoir then work done on System satisfies:

$$W \geq \Delta F$$

and work done by System satisfies

$$W_{by} \leq -\Delta F$$

Where Helmholtz free energy is

$$F = E - TS \text{ in Joules}$$

Proof: Q heat gained / lost by system.

Reservoir heat $Q_{res} = -Q$

Reservoir at constant temperature

$$\Delta S = \frac{Q_{res}}{T_{res}} = \frac{Q_{res}}{T} = -\frac{Q}{T}$$

$$\Delta S + \Delta S_{res} \geq 0$$

$$\Delta S - Q/T \geq 0$$

$$T\Delta S - Q \geq 0$$

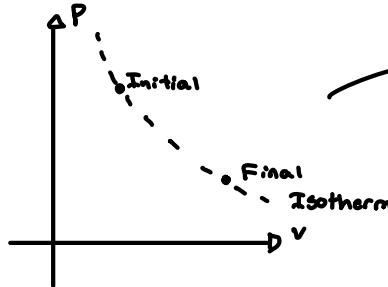
$$\Delta E = W + Q : Q = \Delta E - W$$

$$T\Delta S - \Delta E + W \geq 0 : W \geq \Delta E - T\Delta S$$

$$\begin{aligned} T\Delta S &= T_F(S_F - S_i) \\ &= T_F S_F - T_i S_i \\ &= \Delta(TS) \end{aligned}$$

$$\begin{aligned} W &\geq \Delta E - \Delta(TS) \\ &= \Delta(E - TS) \end{aligned}$$

Scheme



Initial final state have same temp T.

Helmholtz : F.E.

$$F_i = E_i - TS_i$$

$$F_f = E_f - TS_f$$

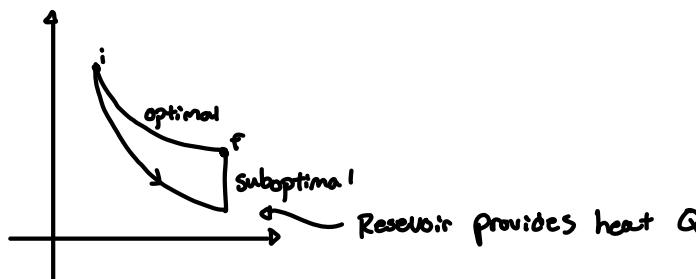
only depend on states

$$\Delta \text{change } \Delta F = F_f - F_i$$

Work done by system is bounded by:
 $W_{\text{by}} \leq -\Delta F$

Optimal work that can be done by a system in contact with a reservoir and whose initial / final states have same temperature as reservoir is an isothermal process and

$$W_{\text{by}} = -\Delta F$$



$$\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{res}}$$

$$= \Delta S - \frac{Q}{T}$$

$$= \frac{1}{T} (T\Delta S - Q) = \frac{1}{T} (T\Delta S - E + W)$$

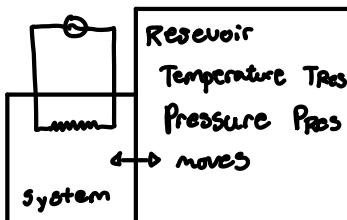
If system does no work

$$\Delta S_{\text{tot}} = \frac{1}{T} (-\Delta F) = -\frac{1}{T} \Delta F$$

System in contact with a reservoir at fixed temperature and which does no work reaches an equilibrium when free energy is a minimum

Gibbs Free Energy

System + reservoir and temperature and pressure of reservoir are fixed



Does work : mechanical work W_{mech}

Can do mechanical work on system

$$W_{\text{mech}} = - \int P \, dV$$

Can also do non-mechanical work on system

W_{non-mech}

total work

$$W = W_{\text{mech}} + W_{\text{non-mech}}$$

If a system is in contact with a reservoir at fixed temperature and pressure and undergoes any process so that initial + final states are in equilibrium with reservoir (Same T,P) then non-mechanical work done on system satisfies

$$\Delta G \leq W_{\text{non-mech}}$$

where Gibbs Free energy is

$$G = E - TS + PV$$

Non-mechanical work done by system satisfies :

$$W_{\text{non-mech by}} \leq -\Delta G$$

If non-mech work is zero then $\Delta S_{\text{tot}} = -\frac{\Delta G}{T}$ System in contact with reservoir at fixed P,T reach equilibrium where G is minimum

2-27-20

Thermodynamic Identities

- Consider heat capacities for any gas

$$dE = dQ - PdV : dQ = dE + PdV$$

i) T,V are independent variables

$$dQ = C_V dT + [\dots] dV$$

$$dE = \left(\frac{\partial E}{\partial T} \right)_V dT + \left(\frac{\partial E}{\partial V} \right)_T dV$$

$$dQ = \left(\frac{\partial E}{\partial T} \right)_V dT + \left[P + \left(\frac{\partial E}{\partial V} \right)_T \right] dV$$

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V$$

ii) T,P are independent variables

$$dQ = C_P dT + [\dots] dP$$

$$\text{need } dV = \left(\frac{\partial V}{\partial T} \right)_P dT + \left(\frac{\partial V}{\partial P} \right)_T dP$$

$$dQ = C_V dT + \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \left[\left(\frac{\partial V}{\partial T} \right)_P + \left(\frac{\partial V}{\partial P} \right)_T dP \right] = \left[C_V + \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right] \right] dV + \dots dP$$

$$C_P = C_V + \left(\frac{\partial V}{\partial T} \right)_P \left[\left(\frac{\partial E}{\partial V} \right)_T + P \right]$$

Calculus rule for differentials

Suppose $f = f(x, y)$

and

$$df = A dx + B dy$$

Know

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy \quad \rightarrow \text{Then } A = \left(\frac{\partial f}{\partial x} \right)_y, B = \left(\frac{\partial f}{\partial y} \right)_x$$

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} : \frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x = \frac{\partial}{\partial y} \left(\frac{\partial f}{\partial x} \right)_y : \left(\frac{\partial B}{\partial x} \right)_y = \left(\frac{\partial A}{\partial y} \right)_x$$

If $f = f(x, y)$ and $df = A dx + B dy$

then

$$A = \left(\frac{\partial f}{\partial x} \right)_y, B = \left(\frac{\partial f}{\partial y} \right)_x$$

and

$$\left(\frac{\partial A}{\partial y} \right)_x = \left(\frac{\partial B}{\partial x} \right)_y$$

Thermodynamic Potentials

Potential - quantity s.t. when differential yields useful physical quantities

uniform gravitational field

$$\begin{array}{l}
 \text{u} = mgy \quad \rightarrow \text{Force components} \\
 \left. \begin{array}{l} F_x = -\frac{\partial u}{\partial x} = 0 \\ F_y = -\frac{\partial u}{\partial y} = -mg \end{array} \right\} \downarrow mg
 \end{array}$$

Potentials in thermodynamics

energy E

entropy S

enthalpy $H = E + PV$

Helmholtz F.e. $F = E - TS$

Gibbs F.e. $G = E - TS + PV$
 $= H - TS$

Fundamental thermodynamic identity

$$dE = T dS - P dV$$

$$ds = \frac{1}{T} dE + \frac{P}{T} dv$$

$$\Rightarrow \frac{1}{T} = \left(\frac{\partial s}{\partial E} \right)_v$$

$$\frac{P}{T} = \left(\frac{\partial s}{\partial v} \right)_E$$

Ex: Suppose that

$s(E, v) = \alpha E^{3/4} v^{1/4}$, where α is a constant. Determine T, v

$$\text{Ans: } \frac{1}{T} = \left(\frac{\partial s}{\partial E} \right)_v = \alpha \frac{3}{4} E^{-1/4} v^{1/4}$$

$$T = \frac{1}{\alpha} \frac{4}{3} E^{1/4} v^{-1/4}$$

$$\frac{P}{T} = \left(\frac{\partial s}{\partial v} \right)_E = \alpha E^{3/4} \frac{1}{4} v^{-3/4}$$

$$P = \alpha \frac{1}{4} T E^{3/4} v^{-3/4} = \alpha \frac{1}{4} \left(\frac{1}{\alpha} \frac{4}{3} E^{1/4} v^{-1/4} \right) E^{3/4} v^{-3/4} = \frac{1}{3} \frac{E}{v} \rightarrow E = 3PV$$

So consider

$$E = E(s, v)$$

then:

$$dE = T ds - P dv$$

$$T = \left(\frac{\partial E}{\partial s} \right)_v$$

$$-P = \left(\frac{\partial E}{\partial v} \right)_s$$

$$\frac{\partial^2 E}{\partial v \partial s} = \left(\frac{\partial T}{\partial v} \right)_s : \frac{\partial^2 E}{\partial s \partial v} = \left(\frac{\partial (-P)}{\partial s} \right)_v : \left(\frac{\partial T}{\partial v} \right)_s = - \left(\frac{\partial P}{\partial s} \right)_v \quad \xrightarrow{\text{Maxwell Equations}}$$

$$C_p = C_v + \left(\frac{\partial v}{\partial T} \right)_p \left[T \left(\frac{\partial P}{\partial T} \right)_v - \cancel{T} + \cancel{P} \right] : C_p = C_v + \left(\frac{\partial v}{\partial T} \right)_p T \left(\frac{\partial P}{\partial T} \right)_v$$

$$C_p = C_v + T \left(\frac{\partial v}{\partial T} \right)_p \left(\frac{\partial P}{\partial T} \right)_v$$

3-3-20

Mathematics for Thermodynamics

* Suppose x, y, z are variables used to describe state of a system

* Some function, f , that only depends on state

* If x, y as independent

$$df = \left(\frac{\partial f}{\partial x} \right)_y dx + \left(\frac{\partial f}{\partial y} \right)_x dy$$

Can show:

$$1) \left(\frac{\partial y}{\partial x}\right)_z = 1 / \left(\frac{\partial x}{\partial y}\right)_z$$

$$2) \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1$$

System Description

Describe states of system using bulk \rightarrow Relationships between these determined via experiments
e.g. P, V, T, N

that describe bulk properties:

$$\text{isobaric expansion coefficient: } \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

Equation of state \rightarrow
e.g. $PV = nRT$ isothermal compressibility: $K = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$

Energy

There exists a thermal energy E that only depends on state of system

First Law of Thermodynamics

$$\Delta E = Q + W, dE = dQ + dW$$

Rule for work e.g. $dW = -PdV : W = - \int PdV$

Heat capacities can be determined experimentally \rightarrow Energy eqn of state, E

$$dQ = C_V dT + [\dots] dV$$

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

LIMITATIONS ON PROCESSES

Second Law:

- * There exists entropy, S, depends only on state
- * Equilibrium state has max entropy subject to constraints
- * Isolated System in any process $\Delta S \geq 0$



Fundamental Thermodynamic Identity

$$\text{e.g. } dE = TdS - PdV + \mu dN \rightarrow dQ = TdS$$



$$\text{Temperature definition } \frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}$$

Thermodynamic Potentials \longrightarrow Maxwell relations, etc, ...

e.g. $G = E - TS + PV$
 $W_{by} \leq -\Delta G$

$$\left(\frac{\partial T}{\partial V}\right)_S = - \left(\frac{\partial P}{\partial S}\right)_T$$